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<p>(54) Title: LAUNDRY BARS HAVING IMPROVED PHYSICAL PROPERTIES</p> <p>(57) Abstract</p> <p>The present invention is directed to a laundry detergent bar composition comprising from about 0.5 % to about 60 % anionic surfactant; from about 0.1 % to about 20 % peroxygen bleach; at least about 14 % phosphate builder, selected from the group consisting of phosphates, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof; and wherein the total moisture content in the final bar composition is from about 0.1 % to about 6 %, and wherein the ratio of the phosphate builder to the total moisture content is from about 4:1 to 12:1.</p>			

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## LAUNDRY BARS HAVING IMPROVED PHYSICAL PROPERTIES

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FIELD

10 The present invention relates to an improved laundry detergent bar composition containing a peroxygen bleach having acceptable physical properties.

BACKGROUND

15 In societies where mechanical washing machines are not common, laundry detergent bars comprising synthetic organic surfactants and detergency phosphate builders are used in the laundering of clothes. Technical developments in the field of laundry detergent bars have concerned formulating bars which are effective in cleaning clothes; which have acceptable sudsing 20 characteristics in warm and cool water and in hard and soft water; which have acceptable in-use wear rates, hardness, durability, and feel; which have low smear; and which have a pleasing odor and appearance. Methods for making laundry detergent bars are also well known in the art. Prior art disclosing laundry bars and methods for making laundry bars include: U.S. Pat. 3,178,370, 25 Okenfuss, issued April 13, 1965; and Philippine Pat. 13,778, Anderson, issued September 23, 1980.

Laundry bar compositions are commonly used in countries having high humidity, such as in the Philippines, India, and Latin America. Consumers often launder clothes outside and therefore often store the laundry bars outside. 30 Although not intended to be limited by theory, such bars which are stored at high humidity conditions tend to absorb moisture in such high humidity conditions. Especially for peroxygen bleach containing laundry bar compositions, the absorption of moisture from high humidity conditions creates bars having unacceptable physical properties due to "puffing" of the bars, making the bar 35 surface wet, soft and covered with small holes.

It has now been found that low-moisture bleach containing bars comprising high levels of phosphate and polyphosphate builder materials have acceptable bar physical properties. As a result, the "puffing" problem is substantially eliminated. Also, the bars have significantly less moisture absorption, especially at high humidity conditions, which leads to a good rate of drying of the surface of the bar. In addition, such bar compositions of the present invention have improved hardness of the bar, thereby retaining the structural integrity during use and transportation. The bar of the present invention is substantially not gritty, meaning that the bar should not be rough to the touch and that the bar should have substantially little hard particles on the surface. Furthermore, such compositions have good bar solubility, and do not easily melt after becoming wet during the washing process. Even further, the bleach in the bars of the present invention are stable.

None of the existing art provides all of the advantages and benefits of the present invention.

#### SUMMARY

The present invention is directed to a laundry detergent bar composition comprising from about 0.5% to about 60% anionic surfactant; from about 0.1% to about 20% peroxygen bleach; at least about 14% phosphate builder, selected from the group consisting of phosphates, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof; and wherein the total moisture content in the final bar composition is from about 0.1% to about 6%, and wherein the ratio of the phosphate builder to the total moisture content is from about 4:1 to about 12:1.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

30

#### DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

35 All percentages are by weight of total composition unless specifically stated otherwise.

All ratios are weight ratios unless specifically stated otherwise.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

5 All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

A. The composition of the present invention comprises from about 0.5% to about 60% anionic surfactant by weight of the total bar composition. Preferably, 10 the bar composition comprises from about 10% to about 50%, more preferably, from about 15% to about 30% anionic surfactant, by weight of the total bar composition.

Anionic surfactants are preferably selected from the group consisting of linear alkyl benzene sulfonate, alkyl sulfate, alkyl ethoxylate sulfate and mixtures 15 thereof.

Anionic synthetic detergent surfactants which are suitable for use herein include the water-soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon 20 atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C<sub>8</sub>-18 carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and 25 potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, 30 abbreviated as C<sub>11</sub>-13 LAS. The alkali metal salts, particularly the sodium salts of these surfactants are preferred. Alkylbenzene sulfonates and processes for making them are disclosed in U.S. Patent Nos. 2,220,099 and 2,477,383.

Mixtures of the above types of anionic surfactants are preferred. Specifically, preferred anionic surfactants are C<sub>10</sub>-18 linear alkyl benzene 35 sulfonates, C<sub>10</sub>-18 alkyl sulfates, and mixtures thereof. C<sub>10</sub>-18 alkyl sulfates can

be in many physical forms, such as paste or flakes; the flake form is preferred. One preferred composition comprises a mixture of LAS:Alkyl sulfate in a ratio of from about 10:90 to about 100:1, preferably from about 20:80 to about 40:60.

B. The composition of the present invention comprises from about 0.1% to 5 about 20% peroxygen bleach, by weight of the total bar composition. Preferably, the bar composition comprises from about 1% to about 10%, more preferably, from about 2% to about 5% peroxygen bleach, by weight of the total bar composition.

The peroxygen bleach of the present invention are those peroxygen 10 bleaching compounds which are capable of yielding hydrogen peroxide in an aqueous solution. These compounds are well known in the art and include hydrogen peroxide and the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates, and the like. 15 Mixtures of two or more such bleaching compounds can also be used, if desired.

Preferred peroxygen bleaching compounds to be used in the present invention include peroxygen bleach selected from the group consisting of perborates, percarbonates, peroxyhydrates, peroxides, persulfates, and mixtures thereof. Specific preferred examples include: sodium perborate, commercially 20 available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Particular preferred are sodium perborate tetrahydrate, and especially, sodium perborate monohydrate. Sodium perborate monohydrate is especially preferred because it is very stable during storage and yet still 25 dissolves very quickly in the bleaching solution.

Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

Other peroxygen bleach agents can also be used such as a percarbonate 30 bleach. Such percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants.

Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

C. The composition of the present invention comprises at least about 14% phosphate builder, by weight of the total bar composition. Preferably, the bar 5 composition comprises from about 14% to about 35%, more preferably, from about 18% to about 25% phosphate builder, by weight of the total bar composition. The phosphate builder is selected from the group consisting of phosphates, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof. Polyphosphates include both cyclic or 10 linear polyphosphates.

The phosphate builders are preferably water-soluble alkali-metal salts of phosphate, including pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof. Preferred phosphate builders are a water-soluble alkali-metal salt of tripolyphosphate, and a mixture of 15 tripolyphosphate and pyrophosphate. Specific preferred examples of phosphate builders include sodium tripolyphosphates (STPP) and tetra sodium pyrophosphates (TSPP), and mixtures thereof.

D. The composition of the present invention has a total moisture content from about 0.1% to about 6%, by weight of the final bar composition. Preferably, the bar 20 composition has a total moisture content from about 1% to about 5%, more preferably, from about 2.5% to about 4.5%, by weight of the total bar composition. The total moisture level of the final bar composition can be determined by any methods known in the art by one skilled in the area of laundry bar compositions. One common method is the Bidwell Sterling Distillation 25 method. Another known method is the Karl Fischer Moisture Titration Method. See AOCS official method Dd2a-59 issue 93 and AOCS official method Dd2b-59 issue 89.

The composition of the present invention has a ratio of the phosphate builder to the total moisture content from about 4:1 to about 12:1. Preferably, 30 the ratio of the phosphate builder to the total moisture content is from about 6.4:1 to about 10:1.

E. Adjunct Ingredients

The detergent bars of the present invention can contain optional surfactants in addition to the anionic synthetic detergent surfactants described 35 above. Such optional surfactants, if present, can be included at levels up to a

total of about 10%, preferably about 0.5-3%, by weight of the total bar composition.

5 A typical listing of the classes and species of optional surfactants, (e.g. nonionic, zwitterionic and amphoteric surfactants) optional alkaline builders such as sodium carbonate trisodium phosphate, etc. and other ingredients useful herein appears in U.S. Pat. No. 3,664,961, issued to Norris on May 23, 1972, and EP 550,652, published on April 16, 1992. Cationic surfactant is another optional surfactant.

10 Amine Oxides are excellent cosurfactants that may be used in conjunction with the present invention. Preferred types are C<sub>12</sub>-C<sub>18</sub> amine oxides, preferably C<sub>14</sub>. If included, the level of amine oxide in the final bar composition is from about 1% to about 10%, preferably, from about 2% to about 5%.

15 Other synthetic anionic surfactants suitable for use herein as additional optional surfactants are alkyl ethoxylate sulfates, the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates. Preparation of alkyl glyceryl ether sulfonates are described in detail in U.S. Pat. 3,024,273, Whyte et al., issued March 6, 1962.

20 In addition, optional synthetic anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and 25 paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

30 In addition, a hydrotrope, or mixture of hydrotropes, may be present in the laundry detergent bar. Preferred hydrotropes include the alkali metal, preferably sodium, salts of toluene sulfonate, xylene sulfonate, cumene sulfonate, sulfosuccinate, and mixtures thereof. Preferably, the hydrotrope is added to the linear alkyl benzene sulfonic acid prior to its neutralization. The hydrotrope, if present, will preferably be present at from about 0.5% to about 5% of the laundry detergent bar.

The builder can optionally contain in addition to the phosphate builder, a non-phosphate detergent builder. Specific examples of non-phosphate, inorganic detergency builders include water-soluble inorganic carbonate and bicarbonate salts. The alkali metal (e.g., sodium and potassium) carbonates and bicarbonates are particularly useful herein. Other specifically preferred examples of builders include polycarboxylates, zeolite, and layered silicates.

Sodium carbonate or sodium hydroxide, another optional ingredient, is particularly preferred as a neutralizing inorganic salt for an acid precursor of an anionic surfactant used in such compositions, such as the alkyl ether sulfuric acid and alkylbenzene sulfonic acid. Co-polymers of acrylic acid and maleic acid are preferred in the subject compositions as auxiliary builders.

Binding agents is particularly preferred to give the bar composition good binding and a good rate of hardening during the manufacture of the bar compositions. Preferably the addition of magnesium sulfate to the bar composition gives such benefits. When used, the bar composition comprises from about 1.5% to about 10%, more preferably, from about 2% to about 5% magnesium sulfate, by weight of the final bar composition. When magnesium sulfate is used, it must be added in the manufacturing process after the addition of both the calcium salt and siliceous material.

Soil suspending agents can be used. Soil suspending agents can also include water-soluble salts of carboxymethylcellulose and carboxyhydroxymethylcellulose. A preferred soil suspending agent is an acrylic/maleic copolymer, commercially available as Sokolan<sup>®</sup>, from BASF Corp. Other soil suspending agents include polyethylene glycols having a molecular weight of about 400 to 10,000, and ethoxylated mono- and polyamines, and quaternary salts thereof. If included, it can be at levels up to about 5%, preferably about 0.1-1%.

A preferred component of the present invention is a chelating agent. Such chelating agents are able to sequester and chelate alkali cations (such as sodium, lithium and potassium), alkali metal earth cations (such as magnesium and calcium), and most importantly, heavy metal cations such as iron, manganese, zinc and aluminum. Preferred cations include sodium, magnesium, zinc, and mixtures thereof.

The chelating agent is preferably selected from a group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof.

One preferred chelating agent is a phosphonate chelating agent, particularly one selected from the group consisting of diethylenetriamine penta(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), and mixtures and salts and complexes thereof, and an acetate chelating agent, particularly one selected from the group consisting of diethylenetriamine penta(acetic acid), ethylene diamine tetra(acetic acid), and mixtures and salts and complexes thereof. Particularly preferred are sodium, zinc, magnesium, and aluminum salts and complexes of diethylenetriamine penta(methylene phosphonate) diethylenetriamine penta (acetate), and mixtures thereof. Also preferred is 1-hydroethoxylidene-1, 1-diphosphonic acid tetrasodium salt, including mixtures, salts and complexes, especially magnesium salts.

Chelating agents have several physical forms, for example liquid chelating agents and dry chelating agents. The dry form of the phosphonate chelating agent is particularly preferred, although the liquid form is also an option. A combination of both liquid and dry form is also preferred. A preferred ratio of liquid to dry chelating agent is from about 70:30 to 0:100, more preferably, 48:52 to 65:35.

Preferably such salts or complexes have a molar ratio of metal ion to chelating agent molecule of at least 1:1, preferably at least 2:1. The detergent chelating agent can be included in the laundry bar at a level of from about 0.1% to about 10%, more preferably from about 0.5% to about 6%, most preferably from about 3% to about 5%.

Another optional component of the laundry bar is fatty alcohol having an alkyl chain of 8 to 22 carbon atoms, more preferably from 12 to 18 carbon atoms. A preferred fatty alcohol has an alkyl chain predominantly containing from 16 to 30 carbon atoms, so-called "high-cut fatty alcohol," which can exhibit less base odor of fatty alcohol relative to broad cut fatty alcohols. Typically fatty alcohol, if any, is present in the laundry bar at up to a level of 10%, more preferably from about 0.75% to about 6%, most preferably from about 2% to about 5%. The fatty alcohol is generally added to a laundry bar as free fatty alcohol. However, low levels of fatty alcohol can be introduced into the bars as impurities or as

unreacted starting material. For example, laundry bars based on coconut fatty alkyl sulfate can contain, as unreacted starting material, from 0.1% to 3.5%, more typically from 2% to 3%, by weight of free coconut fatty alcohol on a coconut fatty alkyl sulfate basis.

5 Another optional component in the laundry bar is a dye transfer inhibiting (DTI) ingredient to prevent diminishing of color fidelity and intensity in fabrics. A preferred DTI ingredient can include polymeric DTI materials capable of binding fugitive dyes to prevent them from depositing on the fabrics, and decolorization DTI materials capable of decolorizing the fugitives dye by oxidation. An example  
10 of a decolorization DTI is hydrogen peroxide or a source of hydrogen peroxide, such as percarbonate or perborate. Non-limiting examples of polymeric DTI materials include polyvinylpyridine N-oxide, polyvinylpyrrolidone (PVP), PVP-polyvinylimidazole copolymer, and mixtures thereof. Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as "PVPI") are also  
15 preferred for use herein. The amount of DTI included in the subject compositions, if any, is about 0.05-5%, preferably about 0.2-2%.

Another optional component in the laundry bar is a fabric softener component. Such materials can be used, if any, at levels of about 0.1% to 5%, more preferably from 0.3% to 3%, and can include: amines of the formula  
20 R<sub>4</sub>R<sub>5</sub>R<sub>6</sub>N, wherein R<sub>4</sub> is C<sub>5</sub> to C<sub>22</sub> hydrocarbyl, R<sub>5</sub> and R<sub>6</sub> are independently C<sub>1</sub> to C<sub>10</sub> hydrocarbyl. One preferred amine is ditallowmethyl amine; complexes of such amines with fatty acid of the formula R<sub>7</sub>COOH, wherein R<sub>7</sub> is C<sub>9</sub> to C<sub>22</sub> hydrocarbyl, as disclosed in EP No. 0,133,804; complexes of such amines with phosphate esters of the formula R<sub>8</sub>O-P(O)(OH)-OR<sub>9</sub> and HO-  
25 P(O)(OH)-OR<sub>9</sub>, wherein R<sub>8</sub> and R<sub>9</sub> are independently C<sub>1</sub> to C<sub>20</sub> alkyl or alkyl ethoxylate of the formula -alkyl-(OCH<sub>2</sub>CH<sub>2</sub>); cyclic amines such as imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher alkyl)imidazoline, where higher alkyl is from 12 to 22 carbons and lower alkyl is from 1 to 4 carbons, such as described in UK Patent Application GB 2,173,827;  
30 and quaternary ammonium compounds of the formula R<sub>10</sub>R<sub>11</sub>R<sub>12</sub>R<sub>13</sub>N<sup>+</sup>X<sup>-</sup>, wherein R<sub>10</sub> is alkyl having 8 to 20 carbons, R<sub>11</sub> is alkyl having 1 to 10 carbons, R<sub>12</sub> and R<sub>13</sub> are alkyl having 1 to 4 carbons, preferably methyl, and X is an anion, preferably Cl<sup>-</sup> or Br<sup>-</sup>, such as C<sub>12</sub>-C<sub>13</sub> alkyl trimethyl ammonium chloride.

Sodium sulfate is a well-known filler that is compatible with the  
35 compositions of this invention. It can be a by-product of the surfactant sulfation

and sulfonation processes, or it can be added separately. Calcium carbonate (also known as Calcarb) is also a well known and often used filler component of laundry bars. Talc is another optional filler material. Filler materials are typically used, if included, at levels up to 40%, preferably from about 5% to about 5 25%.

10 The fabric softening clay is preferably a smectite-type clay that is compatible with the compositions of this invention. The smectite-type clays can be described as expandable, three-layer clays; i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least about 50 meq/100 g. of clay. Preferably the clay particles are of a size that they can not be perceived tactiley, so as not to have a gritty feel on the treated fabric of the clothes. The fabric softening clay can be added to the bar to provide about 1% to about 50% by weight of the bar, more preferably from about 2% to about 20%, and most preferably about 3% to 14%.

15 While any of the smectite-type clays described herein are useful in the present invention, certain clays are preferred. For example, Gelwhite GP is an extremely white form of smectite-type clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% iron (expressed as Fe<sub>2</sub>O<sub>3</sub>) in 20 the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in the instant compositions from the standpoint of product performance. On the other hand, certain smectite-type clays are sufficiently contaminated by other silicate minerals that their ion exchange capacities fall below the requisite range; such clays are of no use in 25 the instant compositions.

30 A Clay flocculating agent is another optional ingredient. Typically such materials have a high molecular weight, greater than about 100,000. Examples of such materials can include long chain polymers and copolymers derived from monomers such as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Gums, like guar gums, are suitable as well. The preferred clay flocculating agent is a poly(ethylene oxide) polymer. The amount of clay flocculating agent, if any, is about 0.2-2%, preferably about 0.5-1%.

35 Optical brighteners are also optional ingredients in laundry bars of the present invention. Preferred optical brighteners are diamino stilbene,

distyrylbiphenyl-type optical brighteners. Preferred as examples of such brighteners are 4,4'-bis[(4-anilino-6-bis(2-hydroxyethyl) amino-1,3,5-triazin-2-yl]amino]stilbene-2,2'-disulfonic acid disodium salt, 4-4'-bis(2-sulfostyryl) biphenyl and 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl) amino]stilbene-2,2'-disulfonic acid disodium salt. Such optical brighteners, or mixtures thereof, can be used at levels in the bar of from about 0.05% - 1.0%.

Dyes, pigments, germicides, and perfumes can also be added to the bar composition. If included, they are typically at levels up to about 0.5%.

Another optional component of the subject invention composition is a photobleach material, particularly phthalocyanine photobleaches which are described in U.S. Patent 4,033,718 issued July 5, 1977, incorporated herein by reference. Preferred photobleaches are metal phthalocyanine compounds, the metal preferably having a valance of +2 or +3; zinc and aluminum are preferred metals. Such photobleaches are available, for example, under the tradename TINOLUS or as zinc phthalocyanine sulfonate. The photobleach components, if included, are typically in the subject compositions at levels up to about 0.02%, preferably from about 0.001% to about 0.015%, more preferably from about 0.002% to about 0.01%.

Titanium dioxide is another optional component. It can be a preferred ingredient for aesthetics of the bar composition, e.g. whiteness.

Another useful optional component of the subject compositions are detergent enzymes. Particularly preferred are lipase, protease, cellulase, amylase, and mixtures thereof. Enzymes, if included, are typically at levels up to about 5%, preferably about 0.05-3%.

#### 25 F. Bar Physical Properties

Although not intended to be limited by theory, when bars are stored in a high temperature and/or a high humidity environment, such as for example 30°C at 80% relative humidity, the bars absorb moisture from the environment. Because of the moisture absorption, the surfactant at the surface of the bar begins to dissolve. As oxygen gas (from the peroxygen bleach) releases towards the surface of the bar, the gas encounters a layer of dissolved surfactant, thereby forming micro bubbles or "puffing" on the surface. The bars of the present invention substantially have no "puffing" of the bars. This means that the bar's surface is smooth and does not have small holes in the surface

that look like indentations. The bars of the present invention are also sufficiently hard and dry even when stored at high temperature and humidity conditions.

A bar physical property of interest is the bar solubility in water. One method of determining the bar solubility is to submerge a bar having the following dimensions: 75mm x 55mm, in 250 ml of water in a beaker for 2 hours, drying the bar at 60 degrees C for 2 hours and then weighing the bar. To have acceptable bar solubility, the difference in weight should be about 15-30 grams for a 120-125 gram bar (12-25% of the original weight of the bar), more preferably 5-25 grams (4-21% of the original weight of the bar).

10 G: Processing

The detergent laundry bars of the present invention can be processed in conventional soap or detergent bar making equipment with some or all of the following key equipment: blender/mixer, mill or refining plodder, two-stage vacuum plodder, logo printer/cutter, cooling tunnel and wrapper.

15 In a typical process the raw materials are mixed in the blender. Alkyl benzene sulfonic acid is reacted with alkaline inorganic salts to complete neutralization, the amount of alkaline inorganic salt being at least sufficient to completely neutralize the acid. At least 5% of the phosphate builder must be present during the neutralization reaction. Preferably at least 10% can be 20 present. Then other optional surfactants followed by any additional optional components such as chelating agents are added. The mixing can take from one minute to one hour, with the usual mixing time being from about two to twenty minutes. The blender mix is charged to a surge tank. The product is conveyed from the surge tank to the mill or refining plodder via a multi-worm conveyor.

25 After milling or preliminary plodding, the product is then conveyed to a two-stage vacuum plodder, operating at high vacuum, e.g. 600 to 740 mm of mercury vacuum, so that entrapped air/gas is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar is preferably cooled, for example in a cooling tunnel, before it is 30 wrapped, cased, and sent to storage. It is preferred that the packed cases of bars be stored at a temperature of 20 - 30°C immediately after packing. Without intending to be limited by theory, this step allows the bars to reach a stable state, physically as well as chemically. After this stabilizing stage, storing the bars at a high temperature and humidity condition should not affect the bar's physical 35 properties and aesthetics.

A preferred laundry bar composition is made by the following method: The raw materials are first mixed in a blender. STPP, sodium carbonate and pre-neutralized CFAS (if a mixture of CFAS/LAS is used as surfactant system) are mixed for about 1-2 minutes. This is followed by the addition of linear alkyl 5 benzene sulfonic acid and sulfuric acid (if present in the formulation). The acids are then completely neutralized by the sodium carbonate in the seat of the blender. (The amount of sodium carbonate should be at least an amount sufficient to neutralize the acids.) Then, a chelating agent, if present is added, followed by other optional surfactants (if present), and any other additional 10 optional components. The total mixing time can take up to about one hour, with the usual mixing time being from about five to twenty minutes. As one of the last ingredients, peroxygen bleach and optionally, enzymes can be added to the mixture and then mixed, preferably, for an additional 2 minutes. It is preferred that when peroxygen bleach is added as one of the last ingredients, the 15 temperature of the blender mixture is about 45 to 65°C. The blender mix is charged to a surge tank. The product is conveyed from the surge tank to the mill or refining plodder via a multi-worm conveyor.

After milling or preliminary plodding, the product is then conveyed to a two-stage vacuum plodder, operating at high vacuum, e.g. 600 to 740 mm of 20 mercury vacuum, so that entrapped air is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar is cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage as described above.

## EXAMPLES 1-6

The following examples further describe and demonstrate the preferred embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration, and are not to be construed as limitations of the present invention since many variations thereof are possible without departing from its spirit and scope.

	1	2	3	
	(weight percent)			
10	Linear alkyl benzene sulfonate	6	0	15
	Coco fatty alcohol sulfate (CFAS)	15	18	0
	C14 amine oxide	0	5	0
	Soda Ash	15	14	15
	Sulfuric acid	2.5	2.5	2.5
15	Sodium Tripolyphosphate	14	18	35
	Calcium carbonate	20	15	10
	Coco fatty alcohol	1	1	1
	Zeolite	2	2	2
	TiO <sub>2</sub>	1	1	1
20	Perborate Monohydrate	2.25	4.5	8
	Fluorescent agents	0.2	0.2	0.2
	Perfume	0.35	0.35	0.35
	Total Moisture Content (final bar)	2.5	2.5	5.0
	Diethylenetriamine pentaacetate	0.9	0.9	0.9
25	Other conventional ingredients	Balance	Balance	Balance
		100	100	100

	4	5	6
	(weight percent)		
5	Linear alkyl benzene sulfonate	6	0
	Coco fatty alcohol sulfate (CFAS)	15	18
	C14 amine oxide	0	5
	Soda Ash	15	15
	Sulfuric acid	2.5	2.5
	Sodium Tripolyphosphate	16	18
10	Calcium carbonate	15	12
	Coco fatty alcohol	1	1
	Zeolite	1	1
	TiO <sub>2</sub>	1	1
	Perborate Monohydrate	2.25	4.5
15	Fluorescent agents	0.2	0.2
	Perfume	0.5	0.5
	Total Moisture Content (final bar)	2.5	2.5
	Chelating agent 1*	2.8	2.8
	Chelating agent 2**	1.5	3
20	Other conventional ingredients	Balance	Balance
		100	100
		100	100

\* Liquid form of preferred chelating agent (diethylenetriamine pentamethylene phosphonic acid)

25 \*\* Dry form of preferred chelating agent (diethylenetriamine pentamethylene phosphonic acid)

30 It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from the scope of the present invention.

## WHAT IS CLAIMED IS:

1. A laundry detergent bar composition comprising:
  - a. from about 0.5% to about 60% anionic surfactant;
  - b. from about 0.1% to about 20% peroxygen bleach;
  - c. at least about 14% phosphate builder, selected from the group consisting of phosphates, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof; and wherein the total moisture content in the final bar composition is from about 0.1% to about 6%, and wherein the ratio of the phosphate builder to the total moisture content in the final bar composition is from about 4:1 to about 12:1.
- 10 2. The laundry detergent bar composition of Claim 1, wherein the composition comprises from about 14% to about 35% phosphate builder.
3. The laundry detergent bar composition of Claim 2, wherein the anionic surfactant is selected from the group consisting of linear alkyl benzene sulfonate, alkyl sulfate, alkyl ethoxylate sulfate and mixtures thereof.
4. A laundry detergent bar composition comprising:
  - a. from about 0.5% to about 60% anionic surfactant selected from the group consisting of linear alkyl benzene sulfonate, alkyl sulfate, alkyl ethoxylate sulfate, and mixtures thereof;
  - b. from about 0.1% to about 20% peroxygen bleach selected from the group consisting of perborates, percarbonates, peroxyhydrates, peroxides, persulfates, and mixtures thereof.
  - c. from about 14% to about 35% phosphate builder, selected from the group consisting of phosphates, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof; and wherein the total moisture content in the final bar composition is from about 1% to about 5%, and wherein the ratio of the phosphate builder to the total moisture content in the final bar composition is from about 6.4:1 to about 10:1.

5. The laundry detergent bar composition of Claim 4, wherein the bar composition further comprises from about 0.1% to about 10% chelating agent.

6. The laundry detergent bar composition of Claim 5, wherein the chelating agent is selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof.

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7. The laundry detergent bar composition of Claim 5, wherein the chelating agent is selected from the group consisting of sodium, zinc, magnesium, and aluminum salts and complexes of diethylenetriamine penta(methylene phosphonate), diethylenetriamine penta (acetate), and mixtures thereof.

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8. The laundry detergent bar composition of Claim 5, wherein the chelating agent has a dry form and a liquid form, and wherein the ratio of liquid form to dry form of the chelating agent is from about 70:30 to about 0:100.

9. A process for making the laundry detergent bar composition of Claim 1, comprising the following steps:

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- a. mixing raw materials for the composition in a blender, wherein at least 5% of the phosphate builder is present during the neutralization of the anionic surfactant;
- b. extruding the mixture of (a); and
- c. forming laundry bars in a conventional manner.

10. A process for making the laundry detergent bar composition of Claim 1, comprising the following steps:

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- a. mixing raw materials for the composition in a blender, wherein at least 5% of the phosphate builder is present during the neutralization of the anionic surfactant;
- b. adding optional ingredients to the mixture of (a);
- c. adding remaining optional ingredients and peroxygen bleach to the mixture of (b) near the end of the mixing process, when the mixture of (b) is from about 45 to 55°C;

10           d. extruding the mixture of (c); and  
              e. forming laundry bars in a conventional manner.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/18006

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 C11D17/00 C11D3/39 C11D3/065 C11D1/37 C11D11/00  
 //C11D1:22, C11D1:29, C11D1:14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>WO 97 44434 A ( THE PROCTER &amp; GAMBLE CO.)          27 November 1997          see page 1, line 35 -- page 4, line 15          see page 5, line 20 -- line 30          see page 7, line 14 -- line 25          see page 9, line 17 -- page 10, line 22          see claims 1,2,4,6,7,9,10</p> <p>---</p>	1-10
X	<p>WO 97 08283 A (THE PROCTER &amp; GAMBLE CO.)          6 March 1997          see claims 1-10          see page 2, line 22 -- page 3, line 2          see page 12, line 1 -- line 13          see page 22, line 33 -- page 23, line 14</p> <p>---</p> <p style="text-align: center;">-/-</p>	1-6

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

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1

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 98/18006

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 27038 A (THE PROCTER & GAMBLE CO.) 12 October 1995 see page 12, line 1 - line 20 see page 16, line 19 - line 32 see claims ----	1-6
X	GB 2 221 220 A (UNILEVER PLC.) 31 January 1990 see claims 1-5 see page 2, line 32 - page 3, line 33 ----	1-4
X	GB 2 172 300 A (UNILEVER PLC.) 17 September 1986 see the whole document ----	1-6
A	GB 2 260 989 A (UNILEVER PLC.) 5 May 1993 see page 1, line 1 - page 4, line 19 see claims; example 6 ----	1-4
A	US 3 562 165 A (ALTIERI RENATO) 9 February 1971 see claims 1-3; examples 1,2 ----	1-4
A	EP 0 312 278 A (UNILEVER PLC.) 19 April 1989 see page 2, line 37 - page 4, line 22 see claims 1-4,9 -----	1-4

# INTERNATIONAL SEARCH REPORT

Detailed information on patent family members

International Application No  
PCT/US 98/18006

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9744434	A	27-11-1997	NONE		
WO 9708283	A	06-03-1997	AU 6780296 A		19-03-1997
WO 9527038	A	12-10-1995	CN 1145093 A CN 1145094 A CN 1145095 A WO 9527036 A WO 9527037 A		12-03-1997 12-03-1997 12-03-1997 12-10-1995 12-10-1995
GB 2221220	A	31-01-1990	IN 170488 A PH 26563 A		28-03-1992 19-08-1992
GB 2172300	A	17-09-1986	BR 8601093 A IN 165353 A JP 1764093 C JP 4053918 B JP 61213300 A		25-11-1986 23-09-1989 28-05-1993 27-08-1992 22-09-1986
GB 2260989	A	05-05-1993	MX 9206243 A ZA 9208404 A		01-04-1993 02-05-1994
US 3562165	A	09-02-1971	DE 1617040 A FR 1522574 A GB 1175749 A JP 48017447 B ES 338432 A		25-02-1971 05-08-1968 23-12-1969 29-05-1973 16-06-1968
EP 0312278	A	19-04-1989	IN 168787 A JP 1132697 A JP 7049598 B		08-06-1991 25-05-1989 31-05-1995

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